EXPERIMENTS AND MODELING OF COAL DEPOLYMERIZATON

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Direct liquefaction of coal is accomplished by the depolymerization of the coal molecule with stabilization of the polymer fragments by hydrogen from coal and the liquefaction solvent. For bituminous coals containing between 80 and 88% carbon, the initial liquefaction reactions produce high molecular weight soluble products and efficiently consume the donatable hydrogens. Up to 80% yields can be produced in short contact time liquefaction (1,2). On the other hand, the production of soluble products from lignites is hindered by crosslinking, resulting in inefficient use of the internal hydrogen and low yields. A correlation between short contact time yields and the crosslink density was discussed by Whitehurst et al (1). As the average crosslink density goes up with decreasing rank, liquefaction yields go down. The crosslink density was determined from solvent swelling ratios (discussed by Larsen and coworkers (3,4).

While there appears to be a higher starting crosslink density in lignites and low rank coals (1-5), many new crosslinks are introduced by reactions starting above 300°C. Suuberg, Lee and Larsen (6) compared pyridine swelling ratios for pyrolysis chars of a lignite and a bituminous coal heated at approximately 1000°C/sec. The results show that lignites crosslink at temperatures (~650 K) far below those where bituminous coals crosslink (800 K). While the tar evolution from bituminous coals is nearly complete before crosslinking begins, crosslinking seems to precede the tar and gas evolution in the case of lignites. In liquefaction, these retrogressive crosslinking reactions reduce the coal's solubility, add thermally stable bonds to the coal structure and consume hydrogen to produce water. Liquefaction of low rank coals could be improved by reducing or eliminating these retrogressive reactions, but little data are available on the mechanisms and relative rates of the crosslinking and bond breaking reactions.

This paper considers the processes of depolymerization and crosslinking under pyrolysis conditions in the absence of a liquefaction solvent. The same depolymerization and crosslinking chemistry which operates in short-contact time liquefaction also controls the yields and molecular weight distributions of the soluble products (tars and liquids) from pyrolyses. In our experimental studies we are determining distributions of depolymerization fragments for coals, lignites, and model polymers (7-11). We consider the factors which control crosslinking such as rank and functional group composition and alteration of the crosslinking reactions by chemical modification of the coal or by variations of the reaction conditions. The results are being used to develop a Monte Carlo devolatilization model including the combined effects of depolymerization, crosslinking and vaporization processes (12).

EFFECT OF CROSSLINKING ON MOLECULAR WEIGHT DISTRIBUTION OF PYROLYSIS PRODUCTS

Field Ionization Mass Spectroscopy (FIMS) has been used to provide the data on the molecular weight distribution of pyrolysis products. In Fig. 3, FIMS spectra for four coals are presented. The detailed shapes of these spectra were discussed in a previous publication (9). These spectra were collected at Stanford Research Institute by direct pyrolysis at 3°C/min into the inlet of the mass spectrometer (13). Since field ionization produces very few fragment peaks, these spectra can roughly be interpreted as the molecular weight distributions of tars. They include single aromatic ring clusters ("monomers") as well as larger coal fragments containing several ring clusters ("oligomers"). It can be seen that the lignite and subbituminous coals have tars with much lower average molecular weights than the spectra for the Illinois #6 and Kentucky #9 bituminous coals. Figure 2 shows a similar dependence with maceral type. The high hydrogen content, fluid macerals produce high molecular weight tars, while the more hydrogen poor macerals produce

lower molecular weight tars. Experiments with coals and model polymers suggest that high molecular weights distributions are characteristic of melting materials and, are often accompanied by high liquid yields because of efficient use of the materials donatable hydrogens. Low molecular weight distributions for tars are characteristic of crosslinked or thermosetting materials with low liquid yields. For low molecular weight tars, more bonds must break and more hydrogen is required to stabilize each gram of product. As discussed in Refs. 7-12 the shape of the molecular weight distribution of pyrolysis decomposition fragments is controlled by the decomposition reactions and by the volatility of the fragments. In the absence of crosslinking, random bond breaking and stabilization by hydrogen abstractions reduce the average molecular weight of the fragments until they are small enough to volatilize. The predicted molecular weight distribution is flat up to the vaporization cutoff. Crosslinking produces two effects, the first is to increase the average molecular weight of fragments, moving many of them above the vaporization limit. The second is to create a network which limits the transport of large fragments out of the reacting coal particle (this network also limits the penetration of solvent and the mobility of coal hydrogen-donor molecules). Both effects lead to the drop off in molecular weight distribution observed for materials which are initially crosslinked or undergo crosslinking during pyrolysis.

MODIFICATION OF THE CROSSLINKING REACTIONS

Modifications of the crosslinking reactions were accomplished in two ways. Pyrolysis experiments were performed (11) on modified coals supplied by Ron Liotta of the Exxon Corporation. In these coals, the hydroxyl and carboxylic acid groups were modified by methylation. Methylation of low rank coals makes their behavior in pyrolysis look like that of easily liquified, fluid, high rank coals. Figure 3 compares the FIMS spectra for a methylated and unmodified coal. The methylated coal produces the high molecular weight distributions, high yields, and fluid properties in agreement with the hypothesis of reduced crosslinking. In a related experiment, very high yields were obtained for a Wyodak subbituminous coal, by Padrick (14), when a strong hydrogen bonding solvent was used. In both experiments the hydroxyl and carboxyl groups which make up the hydrogen bonding network in the coal are tied up (either by methylation or by hydrogen bonds to the solvent) rather than undergoing crosslinking.

The second way in which crosslinking reactions were modified was through control of the reaction conditions. Recent experiments in a heated tube reactor (HTR) at heating rates of 20,000°C/sec (11, 15-17) suggest that in very rapid pyrolyses of lignites the detrimental effects of crosslinking reactions are minimized. In these experiments, the yields of tars are much higher than in low heating rate pyrolyses, the chars have melted and swelled, and the molecular weight distributions of the tars are comparable to those obtained for bituminous coals.

Figure 4 compares scanning electron micrographs of lignite chars produced at 800°C with heating rates of 600°C/sec and 20,000°C/sec. **The 600°C/sec char shows little evidence of fluidity while the 20,000°C/sec HTR char shows fluidity, bubbling, and swelling.**

Figure 5 shows the variation of the molecular weight distribution with high heating rates. Figures 5a and 5b are spectra of tars collected in a heated grid reactor at heating rates of 3 and 600°C/sec, respectively. Figure 5c is a FIMS spectrum of a tar collected in the HTR at a heating rate of 20,000°C/sec. The effect of higher heating rates is to produce tars from lignites which have higher average molecular weights, like the FIMS spectra from higher rank coals (see Figs. 1d and 2c) or methylated coal (Fig. 3b).

FT-IR spectra in Fig. 6 show the tars at high heating rates apparently have not lost their oxygen functionalities as do tars at low heating rates. At low heating rates, these oxygen functional groups are lost in crosslinking reactions accompanied by the evolution of CO, CO_2, and H_2O.

Swelling experiments on chars produced in very rapid pyrolysis confirm that crosslinking reactions in a lignite have been shifted in temperature and no longer precede depolymerization. In Fig. 7 pyridine swelling ratios are compared to tar and liquid (tar plus extract) yields. It can be seen that both crosslinking and tar formation reactions are occurring at about the same rates. These results differ from those of Suuberg et al. obtained at lower heating rates (6). However, for experiments at low heating rates in our laboratory, the swelling ratio went to zero at 300°C (well before any depolymerization can occur), in agreement with the results of Ref. 6. Thus, the sequence of crosslinking followed by tar formation observed for lower heating rates is replaced with simultaneous crosslinking and tar formation at very high heating rates.

POLYMER MODELS FOR COAL STRUCTURE

Model polymers have been used in our laboratory to study the depolymerization and crosslinking reactions believed to occur in coal (7-10,12). Several of the structures studied are illustrated in Fig. 8. For softening coals (no crosslinking), the ethylene-bridged polymers, #1, #3 and #4 were used. The use of this type of polymer allowed examinations of the combined pyrolysis and evaporation processes in a well-characterized material. The tar formation from the polymer has a number of similarities with bituminous coal. Thermal decomposition yields tar consisting of oligomers which, like coal, are similar in composition (except for molecular weight) to their parent polymer. As the original polymer molecular weight is too high for evaporation, tar formation must involve bond breaking. The weak bonds in the polymer system are between the two aliphatic bridge carbons. These ethylene bridges are expected to have bond energies similar to the bonds controlling tar formation in coals. The hydrogens in the ethylene bridges also supply donatable hydrogens for free radical stabilization. Finally, like bituminous coal, these polymers melt prior to tar formation. The vapor pressures for the pure hydrocarbon molecules from the polymers are, however, expected to be higher than for the same size molecules in coals.

A comparison of kinetic rate constants for several of the polymers, some model compounds and coal is presented in Fig. 9. The results show that the bond breaking rate for polymer #1 is similar to that for bibenzyl (18,19), but somewhat lower than that recently measured for coal pyrolysis (10,15,16). The bond breaking rates for the ethylene bridged methoxy-benzene polymer, #2, and an ethylene bridged anthracene polymer, #3, were slightly higher than the formation rate for coal tar. The molecular weight distribution for the naphthalene polymer in Fig. 10a extends to higher masses than for melting coals (as expected due to the higher vapor pressure), but shows similar trends.

The rates of decomposition of ethylene bridged pure hydrocarbon polymers are in reasonable agreement with those for low rank coals, but the molecular weight distributions are quite different. However, the product molecular weight distributions in Fig. 10c for polymer #2, which crosslinks, does show the sharp drop in molecular weight exhibited by low rank coals (Fig. 1a). It is interesting to note that this polymer showed a molecular weight distribution (Fig. 10b) characteristic of a non-crosslinking material (e.g. Fig. 10a) at a lower temperature. The shape changed at higher temperatures, presumably as the crosslinking reactions started.

DEPOLYMERIZATION THEORY OF VAPORIZATION AND CROSSLINKING

The initial reactions occurring during coal liquefaction are thought to involved homolytic cleavage of weak bonds between aromatic rings in coals followed by stabilization of the free radicals by donatable hydrogens from the coal or liquefaction solvent and transport of the products away from the reaction zone (or coal particle) (1,2,20,21). The radicals can also decompose, rearrange, and condense with other radicals or molecules (7,8, 12, 22-24). These secondary reactions lead to the evolution of light gases and to the formation of crosslinks. The processes of

depolymerization, gas evolutions, and crosslinking are thought to be in competition with each other (7,8,12,25). The relative importance of each one is determined by reaction conditions and the availability of donatable hydrogens. These reactions have been studied extensively and modeled for a series of polymers representative of coal structure by Solomon and King (7) and Squire and Solomon (8,12,24). These theories combine random cleavage of weak bonds (similar to the concept used by Gavalas et al. (26) with transport of depolymerization fragments by vaporization and diffusion (like Unger and Suuberg (25) to predict product yields and composition.

The Depolymerization Equation for Ethylene Bridged Polymers – The weak bonds in the depolymerization-vaporization-crosslinking (DVC) theory are the ethylene bridges which homolytically cleave as a first order process with rate constant k_D (see Fig. 9) to form two methyl groups. The radicals which are formed during homolysis of these – CH_2CH_2- bonds are capped by abstracting two hydrogens from a second ethylene bridge. The overall stoichiometry for the depolymerization reaction in the DVC model is, therefore, two ethylene bridges react to form two methyl groups and an olefinic (-CH=CH-) bridge.

The Crosslinking Equation – The crosslinking reaction is modeled as a bond formation between the crosslink sites on any two monomers. Crosslinks between separate sites on the same polymer are allowed. The hydrogens which are freed during this bond formation are modeled as the evolution of H_2 gas. The exact nature of the crosslinking sites in coals is unknown. They could be associated with phenols or carboxylic acid groups or could simply be sites where ring condensations occur. We have found that an important property of crosslink sites is that the probability of having a crosslink site in the molecule goes up with the number of monomers in the molecule. Long polymer chains containing many monomers are more likely to crosslink than are short polymer chains. This behavior leads to tar molecular weight distributions which are characteristic of crosslinking polymers. For the simulations presented in this paper for polymer #4 we have assumed that the crosslinking reaction is first order in the concentration of crosslink sites. The rate constant, shown in Fig. 9 was chosen to make the crosslinking reaction faster than depolymerization at 300°C but slower at 900°C for the benzene polymer #4.

The Vaporization Equations – The vaporization part of the DVC model is treated in the same manner as in the Solomon and King model (7). The rate of vaporization depends on molecular weight, temperature and pressure.

Monte Carlo Simulation Techniques – In solving the DVC model, it is necessary to keep track of the structure of each polymer molecule as bonds break and crosslinks form. This has been accomplished through use of Monte Carlo solution technique. This technique follows a representative sample of polymer molecules through probable pyrolysis reactions. The application of the technique to depolymerization and vaporization of polymers has recently been described (12). In this work we have added crosslinking reactions to the model. The model allows a detailed description of the reaction chemistry involving large numbers of oligomers. For the ethylene bridged polymer, the model keeps track of the concentrations of ethylene and olefinic bridges, methyl groups, crosslink sites, crosslinking bridges, and evolved H_2 gas. The molecular weights of each polymer chain are also continuously monitored in order to determine their volatilities. Examples of these Monte Carlo solutions to the DVC model for the benzene polymer, #4, are presented in Figs. 11 and 12 for a polymer of chainlength 30. The figures show the total number of molecules in each oligomer group ,including smaller and larger masses due to the pressure or absence of methyl groups or hydrogen.

The Effects of Crosslink Site Densities – In Fig. 11 the probability of each monomer containing a crosslink site was varied from 67 to 0%. The heating rate was held constant. The respective char yields decrease from 55 to 0%. In addition, the average molecular weights of the tars increase from 286 to 389 amu. These increased averages for molecular weights are accompanied by higher concentrations of the larger

polymer fragments. This occurs because the probability of a monomer containing a crosslink site is assumed to be equal for every monomer. Long polymer chains contain more crosslink sites and are, therefore, more likely to be lost in crosslinking reactions. The net effect of crosslinking is a preferential decrease in the concentrations of high molecular weight polymer chains and a shift in the tar (those polymer chains which succeed in volatilizing) towards lower average molecular weights. The prediction for 67% crosslinking, Fig. 11a shows the trends of the crosslinked polymer (Fig. 10c) and the low rank coals (Figs. 1a and 3a). The prediction with 0% crosslinks (Fig. 11c) show the trends of the hydrocarbon polymer (Fig. 10a), the high rank coals (Fig. 1d), the methylated coal, Fig. 3b and the high heating rate case (Fig. 5c).

The Effects of Heating Rates - In Fig. 12 the effects of heating rates on tar molecular weight distributions are simulated. The simulations of Figs. 12a-c were carried out for an ethylene bridged benzene polymer in which 67% of the monomers contained crosslink sites. As heating rates are increased from 3 K/min to 20,000 K/s char yields are decreased from 56 to 13% and the fall off in molecular weight occurs at higher values. When pyrolyses are carried out under high heating rate conditions, all of the processes leading to tar formation take place at higher temperatures. These higher temperatures change the relative speeds of the depolymerization, vaporization, and crosslinking processes. As shown in Fig. 9, at high temperatures, depolymerizations are faster than the crosslinking reactions. The net result is that depolymerizations at very high heating rates rapidly reduce the molecular weight of the polymer molecules, making them volatile enough to escape as tar, before the crosslinking reactions can trap them into the char. Char yields are decreased and more dimers, trimers, and tetramers volatilize as tar. In Fig. 12d a tar molecular weight distribution is presented for this polymer when it contains no crosslink sites but is still heated at 20,000 K/s. It can be seen that the shapes and average tar molecular weights of the simulated mass spectra for 20,000 K/s tars are nearly the same with (Fig. 12c) or without (Fig. 12d) crosslink sites. Apparently, at these very high heating rates the effects of the crosslinking reactions are minimized.

These simulations provide an explanation for the changes with heating rates observed in the FIMS spectra of lignite tars, Fig. 5. At low heating rates, Fig. 5a, the FIMS spectrum shows the rapid fall-off with increasing molecular weight which is characteristic of a crosslinking polymer. As heating rates are increased, crosslinking becomes less important and more dimers, trimers, etc. can volatilize. At the very high heating rate, Fig. 5c, the effects of the crosslinking reactions are minimized and the FIMS spectrum of a lignite looks very much like that of a bituminous coal.

CONCLUSIONS

1. In pyrolysis (as in liquefaction) low rank coals undergo crosslinking reactions which reduce the char's fluidity and lead to low yields of low molecular weight soluble products with inefficient use of the coal's internal donatable hydrogen.

2. These reactions can be reduced by methylation or with high heating rates where the coals become fluid and produce higher yields of high molecular weight products.

3. Crosslinking behavior was observed in an ethylene linked benzene polymer containing methoxyl groups. Similar polymers without methoxyl groups do not show the crosslinking behavior.

4. The results have been successfully simulated using a Monte Carlo model for the combined depolymerization, crosslinking and vaporization process.

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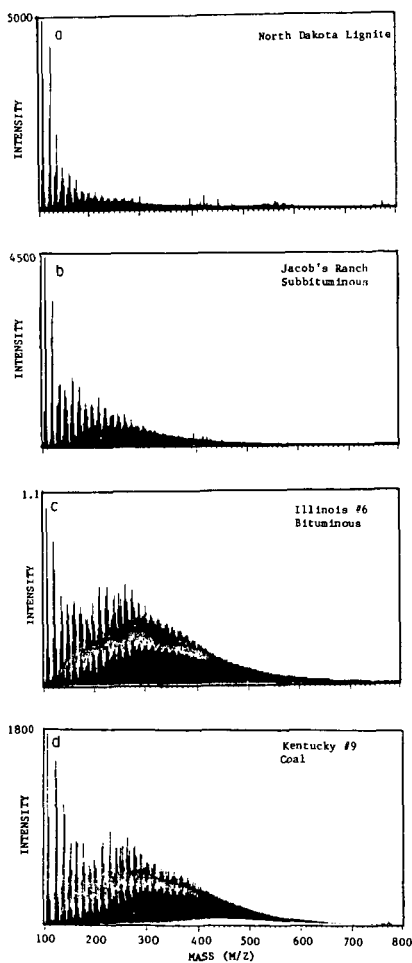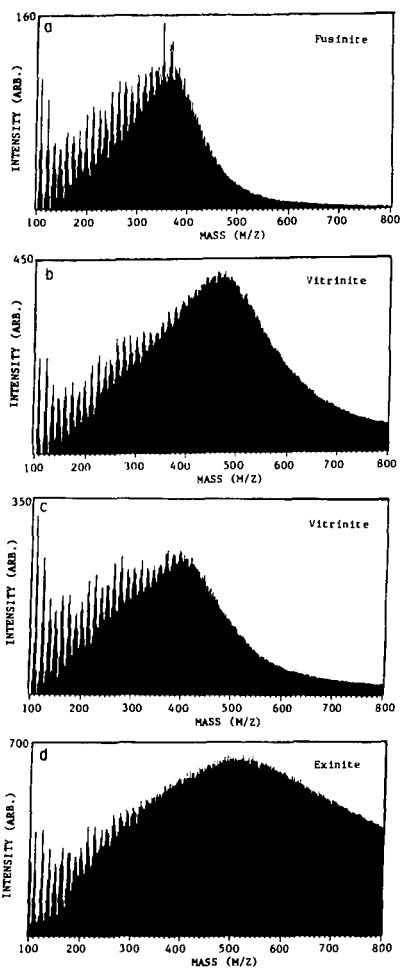
Figure 1. FIMS Spectra of a Lignite and 3 Coals.

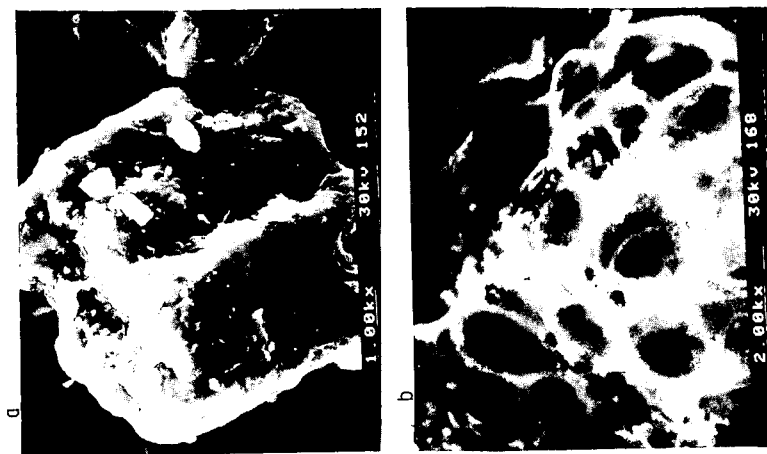Figure 2. FIMS Spectra for Pure Coal Macerals.

Figure 4. Scanning Electron Micrographs of North Dakota Lignite Chars. a) 600°C/sec Heating Rate, and b) 20,000°C/sec Heating Rate.
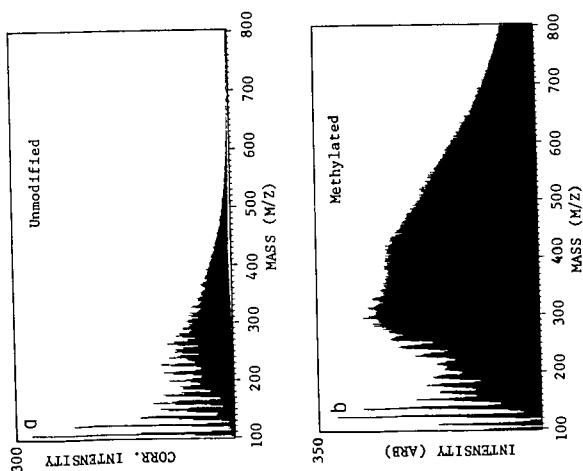

Figure 3. Comparison of FIMS Spectra for Raw and Perdeutero-Methylated Big Brown Texas Lignite.
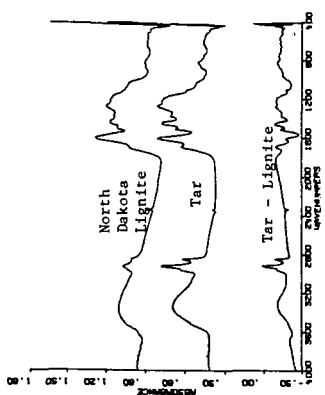
Figure 6. Comparison of FT-IR Spectra of a Lignite and its Pyrolysis Tar. Heating Rate = 20,000°C/sec.
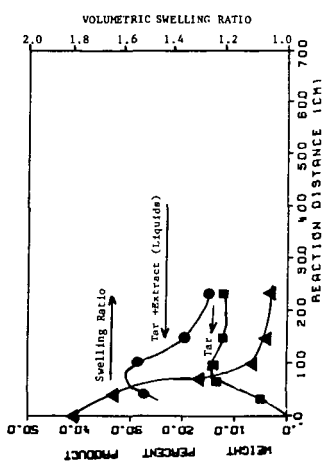
Figure 7. Comparison of Volumetric Swelling Ratios, Tar and Liquid Yields for North Dakota Lignite Heated in the HTR at 800°C.
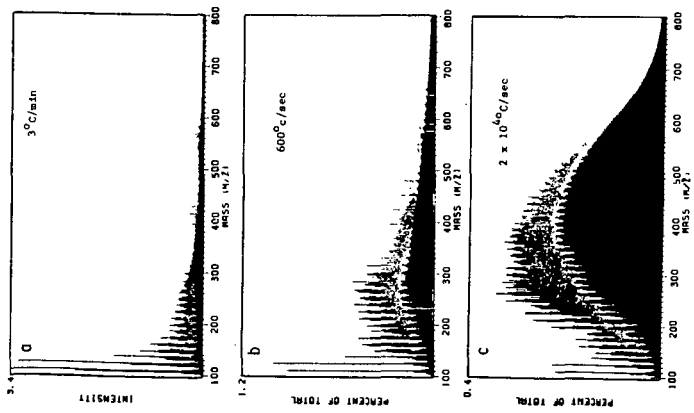
Figure 5. Comparison of Tar Molecular Weights for a Lignite at Three Different Heating Rates.
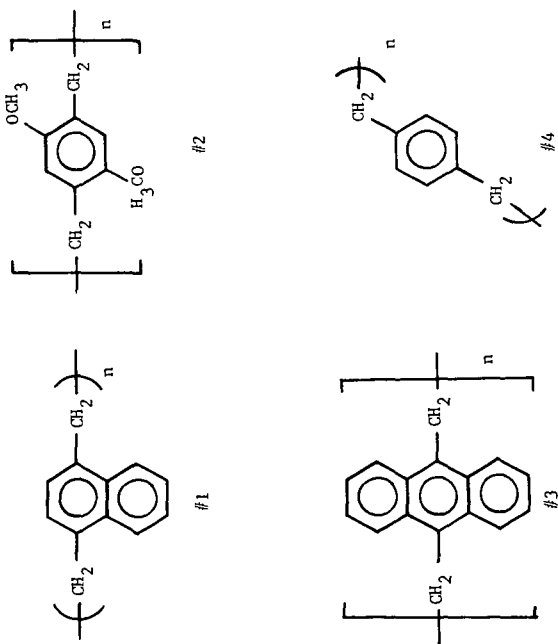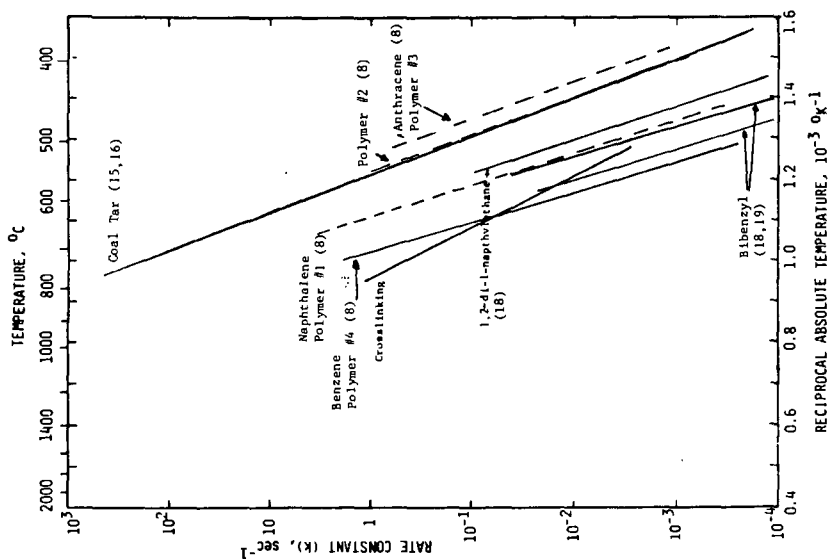
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Figure 9. Comparison of Kinetic Rates for Tar Evolution from Polymers, Coal and Model Compounds.

Figure 8. Model Polymers Already Synthesized or Collected.

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Figure 12. The Effect of Heating Rates on Simulated FIMS Spectra. 1 atm.

Figure 11. The Effect of Crosslink Site Densities on the Simulated FIMS Spectra of Poly(p-xylene). 1 atm, 30K/min.

Figure 10. Comparison of FIMS Spectra for Non-Crosslinking and Crosslinking Polymers.

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